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ELECTRONIC-STRUCTURE STUDY OF THE Na-Ga AND Ni-In INTERMETALLIC
COMPOUNDS USING X-RAY PHOTOEMISSION SPECTROSCOPY

by

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Electronic-Structure Study of the Ni-Ga and Ni-In Intermetallic Compounds Using X-ray Photoemission Spectroscopy

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Polycrystalline Ni-Ga and Ni-In intermetallic compounds of various stoichiometric compositions have been examined by x-ray photoemission spectroscopy. The observed valence-band spectra for all the compounds are very similar to those for elemental Ni; those for Ni_3Ga and NiIn agree rather well with the band-structure calculations of Kubo *et al.* [J.Phys., **F17**, 397 (1987)] and Collinet *et al.* [Z. Metallkd. **77**, 798 (1986), respectively. Only a partial filling of the empty Ni 3d states occurs on forming compounds with Ga or In.

I. INTRODUCTION

The electronic structure of the nickel-metalloid intermetallic compounds has attracted considerable attention in recent years because of their possible application as contacts to III-V semiconductors¹ and their interesting many-body effects compared to elemental Ni.^{2,3} The Ni-Al system has been studied by several groups using x-ray photoemission spectroscopy (XPS)⁴⁻⁷ and ultraviolet photoemission spectroscopy (UPS).⁸ Their results are summarized as follows: with increasing dilution of Ni, (i) the Ni d-band centroid moved to higher binding energy (BE) and the density of states (DOS) at the Fermi level (E_F) decreased; (ii) the Ni d-bandwidth narrowed and the core-level lineshape was more symmetric; and (iii) the satellites in the XPS valence band (VB) and core-level spectra decreased in intensity and shifted to higher BE. The conclusion drawn from these results was that the Ni d-bands were being filled in compounds containing a progressively greater proportion of Al. This filling was assumed to be the result of hybridization of the Ni d-band with the Al sp-band, rather than by actual charge transfer.⁶ However, an x-ray emission study has shown that the filling of the 3d-band in NiAl is not complete.⁹ In addition, some intensity was always observed at the BE of the Ni 2p XPS satellite in the nickel aluminoids, which was interpreted by Hillebrecht *et al.*⁷ as evidence for d-character in the unoccupied states of all the compounds. Studies of the 3d-transition-metal/polyvalent-metal compounds and alloys, such as $(\text{Fe, Co, Ni})_x\text{Al}_{1-x}$ and $\text{Co}_x\text{Ga}_{1-x}$, have confirmed that the main factor governing the electronic structure of these systems is the short-range mixing between the d-states of the transition metals and the sp-states of the polyvalent metals.¹⁰

Recently, a resonant ultraviolet photoemission study² on NiGa showed that the resonantly enhanced VB satellite has about the same intensity as that in elemental Ni, which indicated that the above interpretation by Hillebrecht *et al.*⁷ for the Ni-Al system may also be applied to the Ni-Ga system. Since Al, Ga, and In have the same electronegativity value¹¹ of 1.5, the Ni-Ga and the Ni-In compounds should be similar to the Ni-Al compounds in all their electrical properties. In this study, the XPS spectra of the VB and core levels of all the known compounds



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in the Ni-Ga and Ni-In systems have been investigated to determine if this is indeed the case. The next section of the paper describes the experimental procedure. The experimental results are presented in Sec.III and discussed in Sec. IV. The conclusions drawn from this investigation will be found in Sec. V.

II. EXPERIMENTAL PROCEDURE

The elemental Ni sample used in this study was polycrystalline foil 6 μ m thick and 99.95% pure obtained from Johnson Matthey, Inc. The Ni-Ga and Ni-In intermetallic compounds¹² studied here were prepared by arc melting the constituents together in the required proportions under about 1 atm clean argon in a water-cooled copper hearth. The metals used were of 99.99% purity or better, as specified by the supplier, Johnson & Matthey, Inc. The resulting buttons were remelted five times and, to increase the homogeneity of the samples, were annealed in evacuated quartz tubes at various temperatures. During these processes the total loss of weight was less than 2% for all the samples.

X-ray powder diffraction (XRD) patterns of all the compounds were collected with a Philips diffractometer that utilized Cu K α radiation. Diffraction patterns were obtained by signal averaging for twelve hours to achieve an adequate signal-to-noise ratio to identify minority phases in the materials. From the XRD patterns, most samples contained a single phase, except that the nominal Ni₃Ga₄ and Ni₂Ga₃ compounds were actually mixed phases of each other with about 50:50 composition, and the Ni₂Ga₃ sample contained ~10% of secondary phases.

The XPS spectra were collected with a Kratos ES 800 spectrometer, featuring non-monochromated Al K α radiation ($h\nu=1486.6$ eV) in ultrahigh vacuum (base pressure $\sim 5 \times 10^{-10}$ Torr). The total experimental resolution was estimated to be about 1 eV. The samples were cleaned by cyclic Ar⁺ (3, 2, and 1 kV, 20 mA) bombardment and annealing to 500°C. Although ion bombardment could produce a change of composition or even phase within the XPS sampling depth ($\sim 20\text{\AA}$) via preferential sputtering, subsequent annealing should equilibrate all but the outer

one or two multilayers with the bulk. The XPS spectra were collected with the sample normal pointing into the electron energy analyzer to minimize surface contributions to the spectra. The relative intensities of the Ni and Ga 3d or In 4d XPS lines were measured, and the compound composition within the photoelectron emission depth after ion bombardment and annealing was calculated by using theoretical cross sections.¹³ This calibration agreed with the starting weight of the elements in each sample to within 8% and 19% in the worst cases for the Ni-Ga and Ni-In systems, respectively.¹⁴ The level of contamination was estimated from the intensity of the O 1s and C 1s XPS peaks relative to the Ni peaks and Scofield's calculated photoemission cross sections.¹⁵ The combined O and C contamination on surface was 3 at. % for Ni foil and less than 1 at. % for Ni-Ga and Ni-In compounds in the XPS sampling depth.

III. RESULTS

The XPS spectra presented here are normalized to the same height of the peaks of interest after subtraction of a smooth background¹⁴ and of Al $K\alpha_{3,4}$ satellites. In Fig. 1, XPS VB spectra for elemental Ni and the Ni-Ga intermetallic compounds are presented, while those for Ni metal and the Ni-In intermetallics are shown in Fig. 2.

When a core-level BE is to be measured in a solid, this BE must be defined with respect to some tangible reference level. In a metal, the most easily accessible reference level is the Fermi level, E_F . Unfortunately, when pure metals with different work functions are alloyed, E_F (with respect to the vacuum level, E_v) also shifts by a magnitude often comparable to the observed core-level shifts.¹⁷ A particular core level may not shift at all with respect to E_v upon alloying, but may exhibit a pronounced shift as observed with respect to E_F . At present, however, there is no single measurement capable of referencing the XPS core levels to E_v . Therefore, the reference level problem^{18,19} can be a major difficulty both experimentally and conceptually. In this study, the BE's are referred to E_F , which can be assigned as the 50% point on the high-energy cutoff side of each VB spectrum. Another way of locating E_F is assuming that the instrument and

lifetime broadening function is a Gaussian with a full width at half maximum (FWHM) of 1.4 eV, to move from the 12% point on the high-energy cutoff side to the point at higher BE by one-half of the FWHM of the broadening function. The difference in E_F values determined by these two methods for all the VB spectra presented here are within 0.2 eV. In the present study, the latter method is employed to determine E_F 's for all the spectra. The band positions thus determined and the d-band widths are given in Table I.

Since the Ga and In valence states have low photoemission cross sections in the x-ray region,¹⁵ the VB spectra are dominated by the peak from the Ni d-band. The centroid of this dominant feature is observed to move slightly away from E_F as the proportion of Ga or In in the compounds increases. The widths of these VB spectra are not easily quantified because of the long tails to high BE and, as a consequence, no obvious band narrowing compared with pure Ni was found. This is in marked contrast to the case of PtGa₂ compared with elemental Pt, for which the VB of the compound was less than half the width of the Pt VB.²⁰ The VB satellite, which is located at ~6 eV below E_F , is less intense for the compounds than for pure Ni, and for compounds with lower Ni concentrations these satellites are not observable.

The Ni 2p_{3/2} core peaks and associated satellites for elemental Ni and Ni-Ga compounds and those for elemental Ni and Ni-In compounds are displayed in Fig. 3 and Fig. 4, respectively. These core-level spectra have been shifted to align the Ni 2p_{3/2} main peaks, for which the BE's are summarized in Table II, along with the corresponding satellite positions and intensities. Also shown in Table II are the corresponding values for Ni 2p_{1/2} levels and satellites in the intermetallic compounds studied here. The main 2p lines become narrower and more symmetric as the Ni concentration decreases in the compounds and, at the same time, the satellite separation from the main core peak increases. The satellite intensity for the Ni 2p_{3/2} level, which was determined in the same way as was done in Ref. 7 except a "smooth" (rather than linear) background¹⁶ was subtracted, decreases with increasing dilution of Ni, but such a trend is not obvious for the

Ni $2p_{1/2}$ level. There appears to be no or only small (<0.2 eV) chemical shifts for the Ni 2p levels.

IV. DISCUSSION

Of the compounds studied here, Ni_3Ga and NiIn are the only ones for which the density of states (DOS) have been theoretically calculated. These two compounds were therefore chosen as prototypes in the Ni-Ga and Ni-In systems, in order to compare our XPS data with band structure calculations. To compare them with the XPS spectra, the theoretical DOS were broadened with a Gaussian of 1.4-eV FWHM to simulate instrumental and life-time broadening effects. The broadened DOS and the XPS VB spectra, along with the original DOS, for Ni_3Ga and NiIn are shown in Fig. 5 and Fig. 6, respectively.

The electronic band structure of Ni_3Ga was first calculated by Fletcher²¹ using Hubbard's method in a non-self-consistent scheme. More recently, self-consistent calculations were carried out by Hayden *et. al.*,²² using the linear muffin-tin orbitals (LMTO) method, and by Kubo and Wakch,²³ using the symmetrized augmented plane waves (SAPW) method. The latter calculations showed that the one-electron d-band width of Ni_3Ga is narrower than that calculated by Fletcher. Our FWHM of the XPS VB of Ni_3Ga (3 eV) agrees with the theoretical value of Kubo and Wakch (~ 2.9 eV). The dominant feature in the Ni_3Ga XPS VB spectrum arises from electrons in the non-bonding Ni d-orbitals. The bonding states, which form from the hybridization of Ni 3d and Ga 4p electrons, are not resolved separately in the XPS spectrum.

Colinet *et. al.*,²⁴ using the cluster Bethe lattice method, calculated the DOS of NiIn stoichiometric compound. In their calculation, strong sp-d hybridization produces a pseudogap at the top of the d-band. In Fig. 6, the peak in the DOS located just below the pseudogap is caused by the very weakly coupled d-states, while the strongly mixed d-sp-states are characterized by the higher binding energy peak and by the group of states that lie above the pseudogap. The XPS VB spectrum agrees quite well with the broadened DOS curve from this calculation. However, the

higher binding energy peak is not resolved in the XPS spectrum, and the total d-bandwidth is underestimated by the calculation. This underestimation of the theoretical bandwidth compared to the XPS data of NiIn was also noticed by Hillebrecht *et al.*⁷ in their XPS data of NiIn and band-structure calculation, in which they used the augmented spherical waves (ASW) method. This indicates that the disagreement between theory and experiment for the bandwidth of NiIn is independent of the theoretical methods used.

An important point to note is that all of the above band-structure determinations were one-electron calculations. Since the 6-eV satellite peaks observed in the XPS VB spectra do not show up in the theoretical DOS curves of Ni₃Ga and NiIn, these features are most likely the result of many-electron transitions. For both the Ni₃Ga and the NiIn cases, there is considerable photoemission intensity in the 6- to 8-eV binding energy regions of the spectra that is not present in the theoretical DOS calculations.

Because the DOS at E_F ($n(E_F)$) in pure Ni is one order of magnitude higher than $n(E_F)$ in pure Ga and In,²⁵ a decreasing Ni concentration causes a decrease of $n(E_F)$ in the compounds studied here. In other studies,^{6,7} it was possible to correlate a decrease in XPS intensity at E_F for many Ni alloys with a decrease in the electronic specific heat and the $n(E_F)$ value. Unfortunately, Ni₃Ga is the only compound studied here for which the specific-heat data are available. The $n(E_F)$ values in states/eV-atom obtained from theoretical calculations (1.36, 1.56, 1.61 in Refs. 23, 22, 21, respectively) are substantially lower than those obtained from specific-heat measurements (2.54, 3.54, 4.13, in Refs. 26, 27, 28, respectively). Since the experimental data were not corrected for the electron-electron and electron-phonon mass enhancements in deriving $n(E_F)$ values, this discrepancy may be caused by the enhanced magnetic fluctuations²⁹ in Ni₃Ga, which were also observed³⁰ in Ni₃Al. Choosing the experimental $n(E_F)$ value of 2.54 for Ni₃Ga (Ref.29) and comparing it with the value of 2.97 for Ni (Ref.31) yields an 85% decrease in this value from Ni to Ni₃Ga, which is comparable to the 76% decrease in the XPS intensity at E_F relative to the maximum of the d-band.

The I_{sat} value (satellite intensity as a percentage of total intensity of main line plus satellite) for the Ni $2p_{3/2}$ level in Ni metal in this study is 19%, which is much smaller than those reported previously by Hillebrecht *et al.* (29%),⁷ Stadnik *et al.* (29%),³² and Kulkarni *et al.* (27%).³³ However, there are two I_{sat} values in the literature that are close to the value obtained in the present study. One is that of Torrisi *et al.*³⁴ ($I_{\text{sat}} \sim 18\%$) for a Ni strip, and the other is that of Thube *et al.*³⁵ ($I_{\text{sat}} \sim 20.4\%$) for a Ni foil. In order to see the effect of data analysis on the I_{sat} value, various methods have been used in analyzing our Ni film data, including a linear background subtraction with or without subtracting the Al $K\alpha_{3,4}$ satellite. A maximum value of $I_{\text{sat}} = 21\%$ was obtained. One point worth noting is that our I_{sat} values (within the uncertainty of 2%) for Ni $2p_{3/2}$ levels in NiIn and Ni₃Al are the same as those reported in Ref. 7. We do not understand the origin for this discrepancy among I_{sat} values (for the Ni $2p_{3/2}$ level of elemental Ni) reported so far. However, accepting our I_{sat} value for Ni metal, one does not observe a "sharp" decrease in the Ni $2p_{3/2}$ satellite intensity with decreasing Ni concentration in the Ni-Ga and Ni-In systems. For narrow-band metals, the satellite intensity depends not only on the number of empty d-states but also on the d-bandwidth, the intra-atomic Coulomb interaction, and the detailed band structure.³⁶ Thus, it is difficult to extract quantitative conclusions from the I_{sat} value concerning the d-band filling in these compounds. Qualitatively, it appears that the Ni empty d-states are filled incrementally when they are forming Ni compounds with increasing amounts of Ga or In. In agreement with the resonant photoemission study² of NiGa, this study showed that the Ni 3d-band in the Ni-Ga and Ni-In compounds is only partly filled, even at the highest metalloid concentrations.

Although there is no fully satisfactory quantitative theory for dealing with correlation effects within the d-band,³⁷ several theoretical studies using the Hubbard model³⁸ identified the XPS core-level satellites of Ni as a two-hole bound state, which is the result of a photoemission event that leaves a localized 3d hole on the site of a previously existing core hole. There are no corresponding satellites on the high BE side of the Ga 3d or In 4d XPS peaks, from which one

can deduce that all the Ni satellites in the compounds are intrinsic and localized at the same Ni atom. This confirms the nature of the XPS satellites as studied theoretically within the Hubbard model.

It is well understood that the asymmetry of transition-metal XPS lineshapes arises from excitations of electron-hole pairs at E_F , and that the severity of the asymmetry increases with the local joint DOS for electron-hole pair excitations.³⁹ The Ni 2p lines for the compounds studied here are more symmetric than those for elemental Ni, which provides an independent confirmation of the decrease of $n(E_F)$ for the intermetallics. Since the Ni $2p_{3/2}$ satellite has a multiplet structure and some of its components are very close to the main $2p_{3/2}$ line, a quantitative analysis of the line asymmetry is difficult. The overlap of the Ni $2p_{3/2}$ line and its satellite causes the apparent energy separation between them to be smaller than that of the Ni $2p_{1/2}$ line and its satellite.⁴⁰

In general, XPS core-level chemical shifts can be related to the amount of charge transfer among the atoms,⁴¹ which in the cases studied here is expected to be small because the electronegativities of Ni, Ga and In are very similar.¹¹ The chemical environment of the atoms determines the charge density, which affects the orbital energies of the initial-state electrons as well as the relaxation energies of the final state, owing to the response of the conduction electrons to the hole created by the photoemission process. In the compounds studied in this paper, no large chemical shifts were found. This is not surprising, since the charge transfer is usually small in intermetallic compounds,⁷ and the opposing effects of charge transfer and relaxation nearly cancel.⁴²

V. CONCLUSIONS

XPS VB and core-level spectra of nine Ni-Ga and Ni-In intermetallic compounds of various stoichiometric compositions have been investigated. As the Ni concentration decreases, a slight filling of the Ni d-band is supported by the following:

- (i) the VB peak moves to higher BE;
- (ii) the intensities of the satellites of the VB and the Ni $2p_{3/2}$ XPS peaks decrease and the separations from the main peak increase; and
- (iii) the Ni $2p_{3/2}$ XPS core peak becomes less asymmetric.

However, the XPS data from this work show that compound formation with Ga or In fills the Ni 3d-band only partially, since the Ni 2p satellite was always observed and the decrease of the satellite intensity from elemental Ni to the Ni compounds was smooth. To prove that there is d-character in the unoccupied states, which was proposed by Hillebrecht *et al.*⁷ to interpret their XPS data of NiAl, high-resolution inverse-photoemission studies on the Ni-metalloid compounds may be helpful.

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 14. The compound compositions within the XPS sampling depth ($\sim 20\text{\AA}$) calculated from the Ni and Ga 3d (In 4d) intensities and the theoretical cross sections of Ref. 13 are as follows:
 Ni_3Ga ($\text{Ni}_{0.76}\text{Ga}_{0.24}$), Ni_3Ga_2 ($\text{Ni}_{0.58}\text{Ga}_{0.42}$), NiGa ($\text{Ni}_{0.52}\text{Ga}_{0.48}$),
 Ni_3Ga_4 ($\text{Ni}_{0.49}\text{Ga}_{0.51}$), Ni_2Ga_3 ($\text{Ni}_{0.48}\text{Ga}_{0.52}$), Ni_3In ($\text{Ni}_{0.80}\text{In}_{0.20}$),
 $\text{Ni}_{13}\text{In}_9$ ($\text{Ni}_{0.74}\text{In}_{0.26}$), NiIn ($\text{Ni}_{0.69}\text{In}_{0.31}$), Ni_2In_3 ($\text{Ni}_{0.56}\text{In}_{0.44}$),
 where the compositions inside the parentheses are those obtained from XPS peak intensities.
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Table I. Valence-band properties in Ni-Ga and Ni-In intermetallic compounds
(all values in eV with respect to the Fermi energy).

Compound	Peak BE ^a	FWHM ^b	Satellite BE ^c
Ni	1.0	3.08	5.9
Ni ₃ Ga	1.0	3.04	
Ni ₃ Ga ₂	1.2	3.16	5.8
NiGa	1.2	3.19	5.9
Ni ₃ Ga ₄	1.2	3.14	<i>d</i>
Ni ₂ Ga ₃	1.2	3.13	<i>d</i>
Ni ₃ In	1.0	3.27	5.9
Ni ₁₃ In ₉	1.0	3.2	5.4
NiIn	1.0	3.2	5.4
Ni ₂ In ₃	1.3	3.9	<i>d</i>

a. Uncertainty ± 0.2 eV

b. Uncertainty ± 0.4 eV

c. Uncertainty ± 0.6 eV

d. Satellite too weak for reliable estimate

Table II. Binding energies of Ni $2p_{1/2}$, $2p_{3/2}$ levels and satellites in Ni-Ga and Ni-In intermetallic compounds (in eV).

	$2p_{3/2}$ BE ^a	ΔE^b	I_{sat}^c	$2p_{1/2}$ BE ^a	ΔE^b	I_{sat}^c	Chemical shift ^d
Ni	852.8	5.4	18.7	870.1	4.4	24.0	
Ni ₃ Ga	852.8	5.9	16.6	870.1	4.6	22.3	0
Ni ₃ Ga ₂	852.7	5.7	17.9	870.0	4.8	26.3	-0.1
NiGa	852.6	6.2	16.0	869.9	4.9	27.2	-0.2
Ni ₃ Ga ₄	852.9	6.7	15.3	870.0	5.2	25.4	0
Ni ₂ Ga ₃	853.0	6.7	14.4	870.2	4.9	25.0	+0.1
Ni ₃ In	852.8	5.6	17.6	870.1	5.1	25.9	0
Ni ₁₃ In ₉	852.8	5.6	18.1	870.0	4.6	25.0	-0.1
NiIn	852.7	6.1	18.7	869.8	5.2	24.0	-0.2
Ni ₂ In ₃	852.8	7.0	11.1	870.0	5.2	22.9	-0.1

a. Uncertainty ± 0.2 eV.

b. Binding energy difference between main line and satellite; satellite has larger binding energy. Uncertainty ± 0.4 eV.

c. Satellite intensity as percent of total intensity of main line plus satellite. Uncertainty $\pm 2\%$.

d. BE(intermetallic compound)- BE(Ni), averaged over 2p lines. Uncertainty ± 0.4 eV.

FIGURE CAPTIONS

Figure 1. XPS VB spectra from the Ni-Ga intermetallic compounds. The intensities of all spectra have been normalized to the peak maxima.

Figure 2. Same as in Fig. 1 except from the Ni-In intermetallic compounds.

Figure 3. Ni $2p_{3/2}$ XPS spectra from Ni-Ga intermetallic compounds, normalized to constant peak height and shifted to align the main peaks. The arrows indicated the peak positions of the 6-eV satellite.

Figure 4. Same as in Fig. 3 except from the Ni-In intermetallic compounds.

Figure 5. (a) Valence band density of states for NiGa. Circles are the experimental XPS spectra collected in this study corrected for a smooth background and Al $K\alpha_{3,4}$ satellites. The dashed curve is from the calculation of Fletcher [Ref. 21], and the solid curve shows the theoretical curve broadened with a Gaussian to simulate the experimental resolution and lifetime broadening effects (1.4-eV FWHM).
(b) Same as in part (a) except the dashed curve is from the calculation of Kubo and Wakch [Ref. 23], and the solid curve is the theoretical result after broadening (1.4-eV FWHM) with a Gaussian.

Figure 6. Valence band density of states for NiIn. Circles are the experimental XPS spectra collected in this study, corrected for a smooth background and Al $K\alpha_{3,4}$ satellites. The dashed curve is from calculations by Colinet *et al.* [Ref. 24], and the solid curve represents the theoretical curve Gaussian broadened by 1.4-eV FWHM.

FIGURE CAPTIONS

Figure 1. XPS VB spectra from the Ni-Ga intermetallic compounds. The intensities of all spectra have been normalized to the peak maxima.

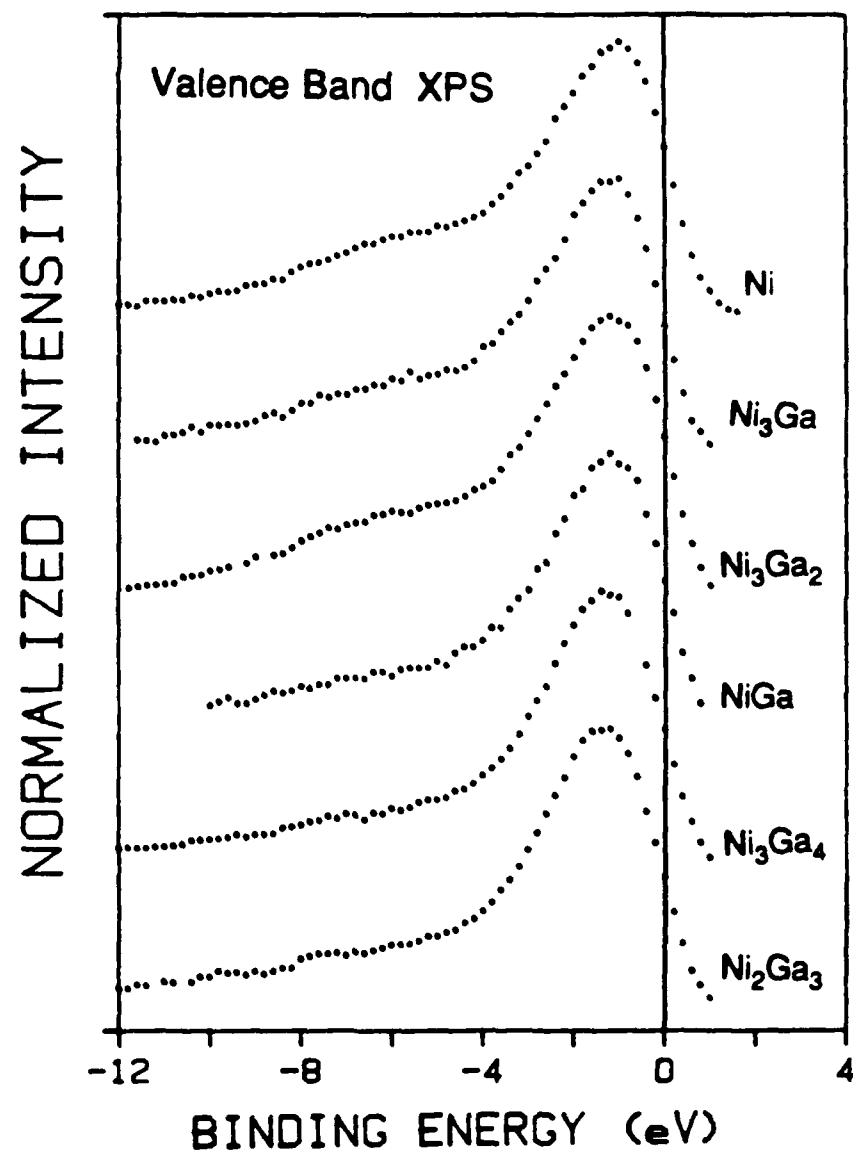
Figure 2. Same as in Fig. 1 except from the Ni-In intermetallic compounds.

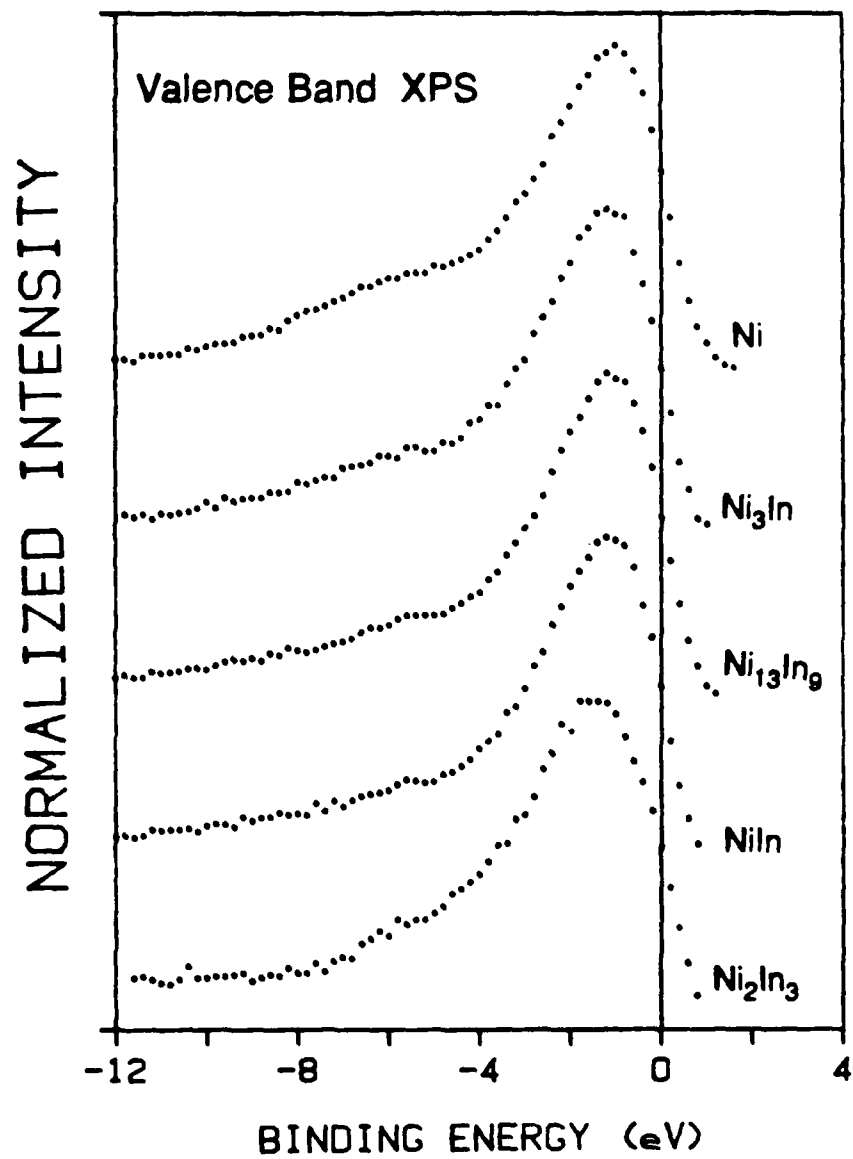
Figure 3. Ni $2p_{3/2}$ XPS spectra from Ni-Ga intermetallic compounds, normalized to constant peak height and shifted to align the main peaks. The arrows indicated the peak positions of the 6-eV satellite.

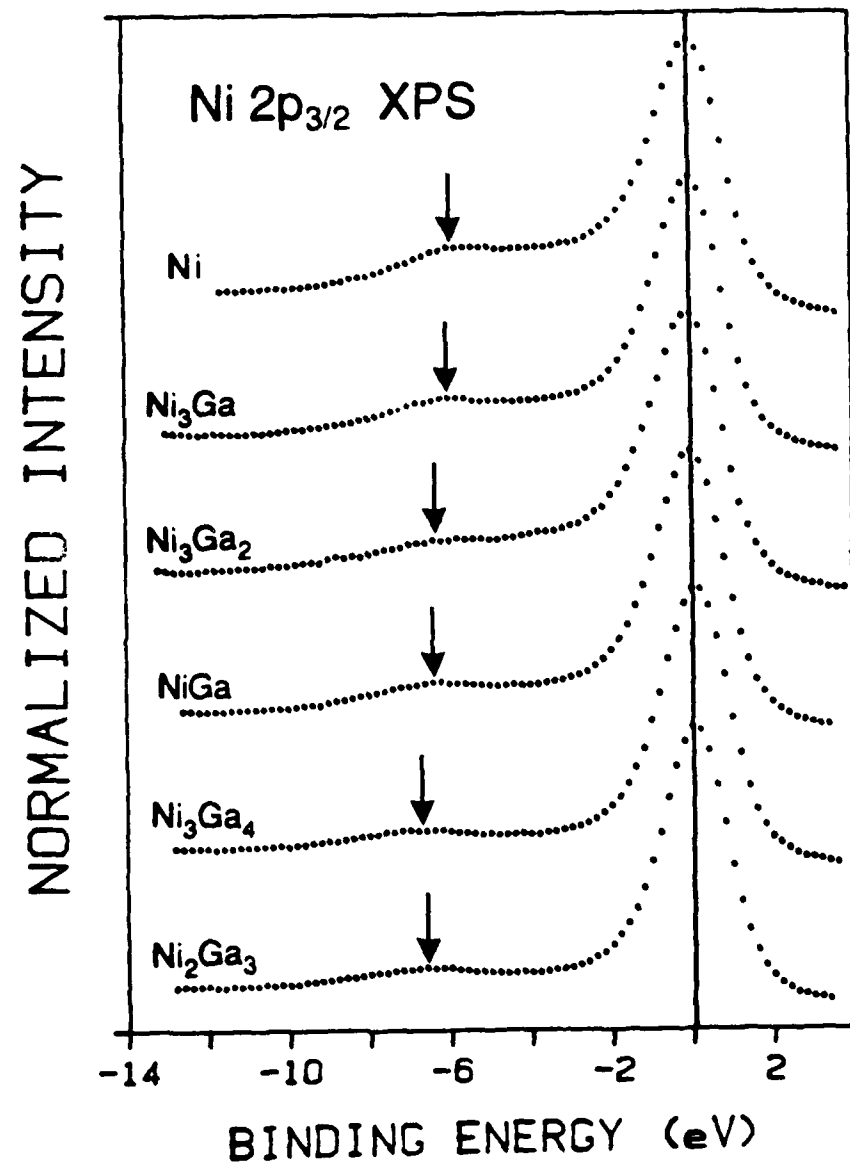
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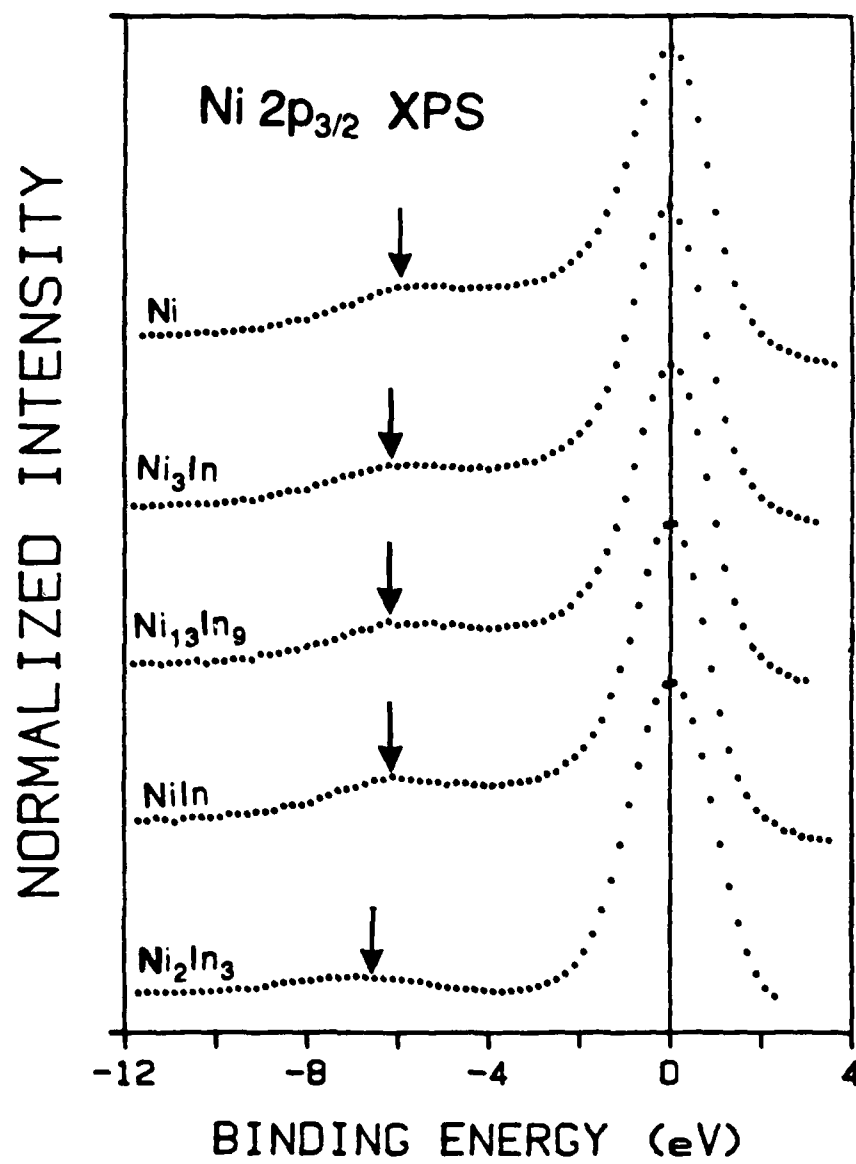
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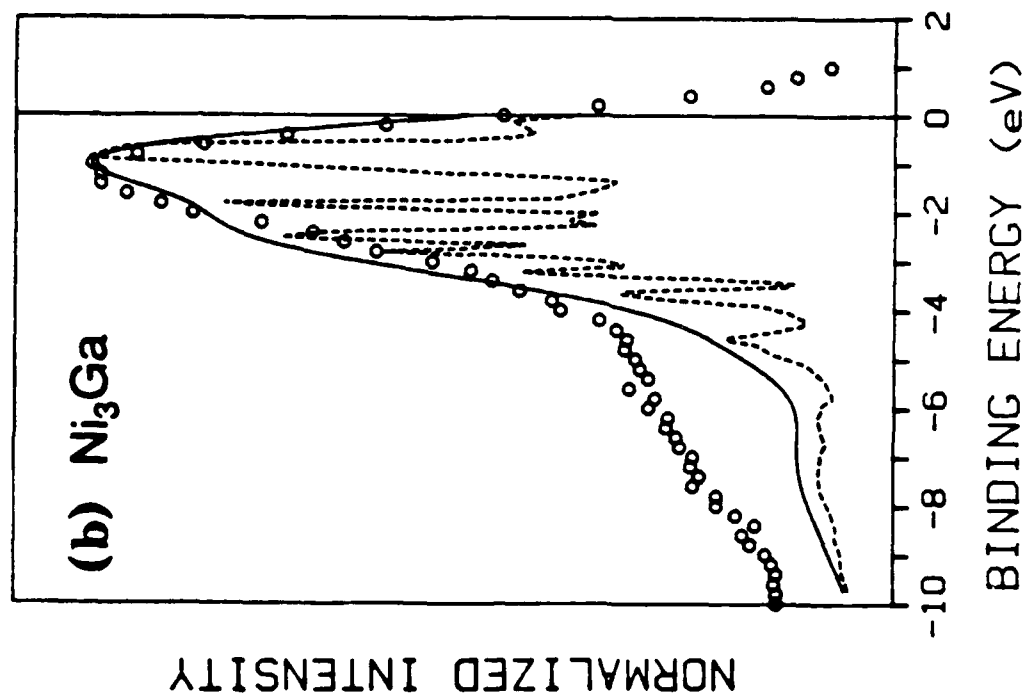
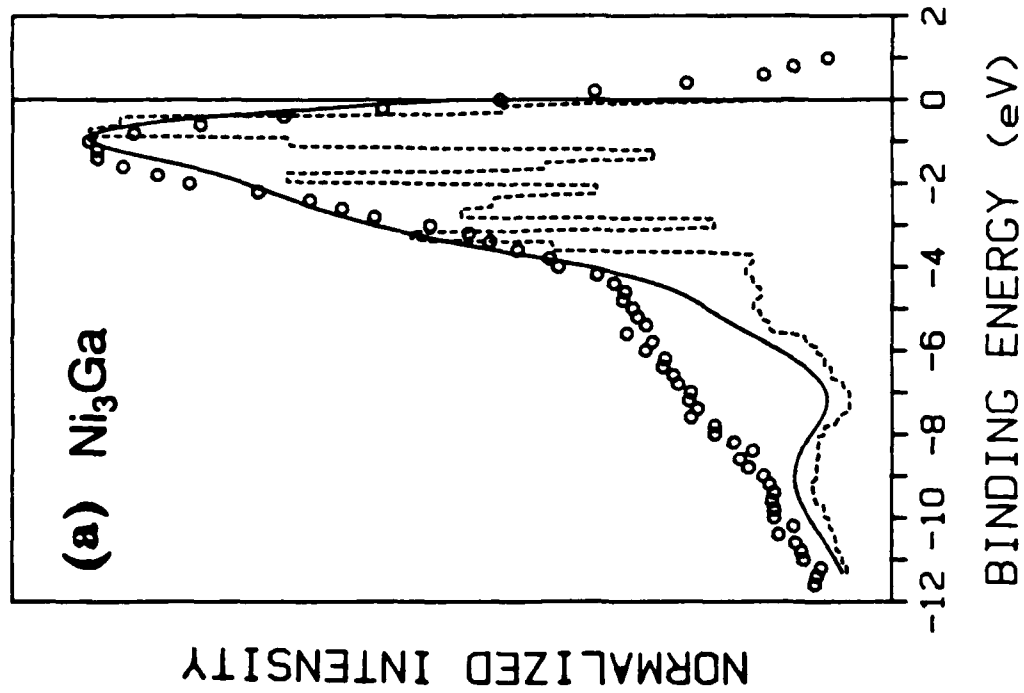
Figure 6. Valence band density of states for NiIn. Circles are the experimental XPS spectra collected in this study, corrected for a smooth background and Al $K\alpha_{3,4}$ satellites. The dashed curve is from calculations by Colinet *et al.* [Ref. 24], and the solid curve represents the theoretical curve Gaussian broadened by 1.4-eV FWHM.

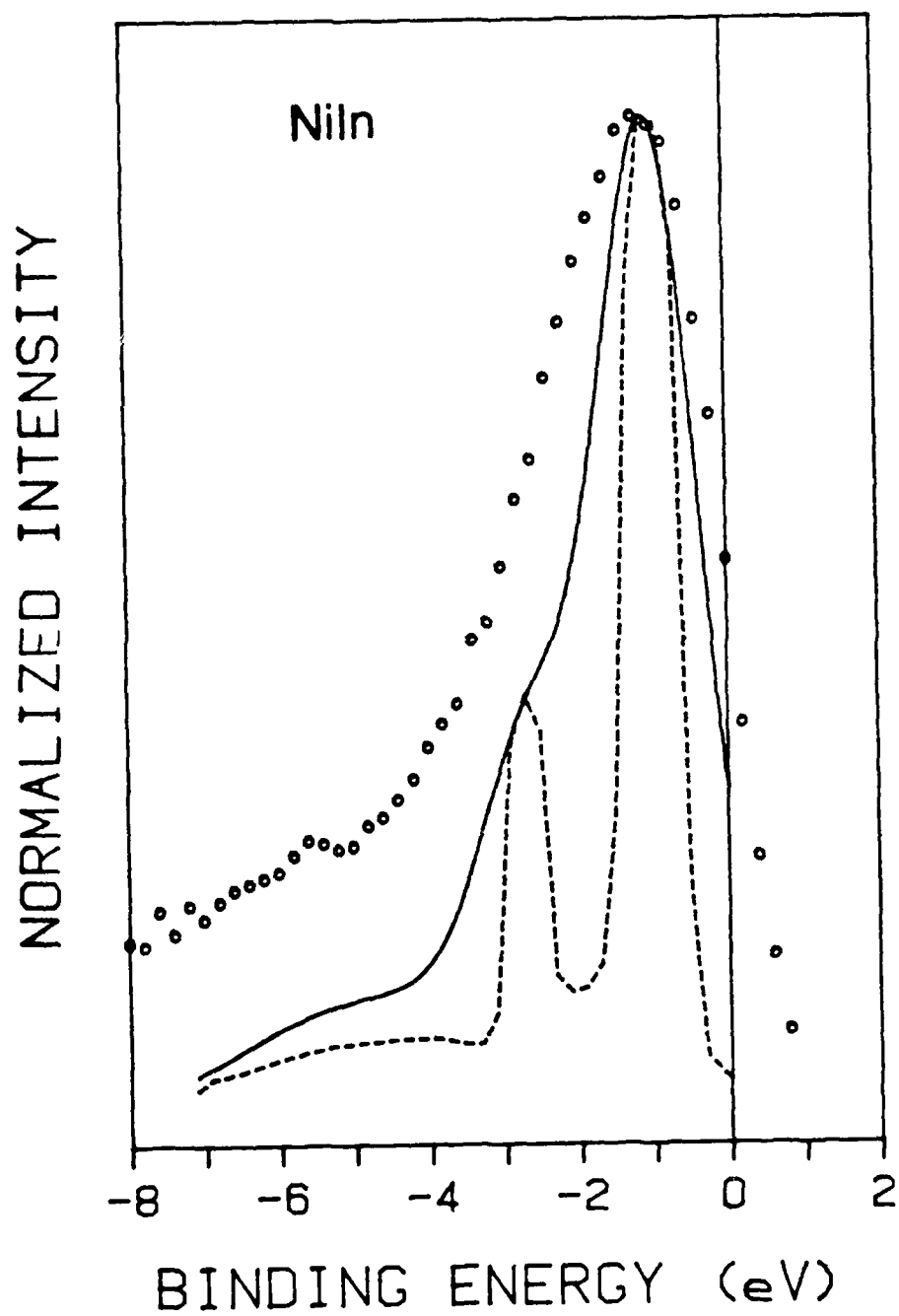












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